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OF A PRELIMINARY PASSIVATION

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# INCREASE OF COHESIVE STRENGTH OF METALLIC COATINGS BY MEANS OF A PRELIMINARY PASSIVATION

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The results of a quantitative investigation of the influence of passivation on the cohesive strength of metallic coatings are presented. Data on the effect of passivation on the cohesive strength of hot coatings are also given.

The strength of cohesion between metallic coatings and the base material /1956\* is one of the principal indicators of their quality. The cohesive strength essentially influences the protecting properties of coatings, and determines their usefulness in repair work.

We have shown earlier (Ref. 1) that a preliminary passivation before the application of coatings lowers porosity, heightens the resistance of coatings to corrosion, and enhances the strength of cohesion between them and the base metal.

In our articles which have been published earlier, we have presented only fragmentary qualitative data on the effect of a preliminary passivation on the cohesive strength of electro-deposited coatings.

In the present article we shall report on the results of a quantitative investigation of the influence of passivation on the cohesive strength, and also data on the effect of passivation on the cohesive strength of hot coatings.

We have tested copper, nickel, iron, and aluminum coatings on steel.

In order to determine quantitatively the strength of cohesion between /1957 nickel and copper coatings on steel, we have adopted a method in which a strip of coating 50  $\mu$  in thickness was broken off under the influence of a gradually increasing load. This technique, and the calculation method were earlier used by Jaquet (Ref. 2), and Gorbunova and Zhukova (Ref. 3).

The copper coatings were deposited in the standard sulphate electrolyte (g/l):  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  - 200,  $\text{H}_2\text{SO}_4$  - 50 with the current density  $i_k = 1$  A/square decimeter; the nickel coatings were deposited in an electrolyte having the content (g/l):  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  - 180,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  - 40,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  - 45,  $\text{H}_3\text{BO}_3$  - 20,  $\text{NaCl}$  - 7. The current density was  $i_k = 0.8$  A/square decimeter.

The passivation of steel specimens was conducted in concentrated nitric acid (specific gravity 1.36) at 4-8°C, or in a passivating solution with the content (g/l):  $\text{NaOH}$  - 150,  $\text{NaNO}_2$  - 300,  $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$  - 5. The temperature of

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\* Numbers in the margin indicate pagination in the original foreign text.

the solution during passivation was 106-114°; the duration of the treatment was 8-12 seconds.

During the breaking off of the copper coating, which was deposited from the acid copper bath onto the surface of steel specimens, prepared by usual methods, the values of the limiting load -- at which the copper coating 1 cm in width was broken off -- ranged from 350 to 650 g/specimen. The average value of the work needed to break the copper coating off of the non-passivated steel specimens amounted to  $0.63 \cdot 10^6$  erg/cm<sup>2</sup>. The copper coatings, deposited onto steel specimens passivated in nitric acid, did not break off the surface of the latter. After we had reached the load value of 1770-2000 g, the copper strip cracked along the width of the specimen. In this process, the average value of the break-off work was  $1.73 \cdot 10^6$  erg/cm<sup>2</sup>.\*

The nickel coatings, deposited onto the surface of steel specimens, prepared by the usual methods, were broken off at the limiting load values of 700-1000 g/specimen for the majority of cases, and at 2500-3000 g/specimen for several specimens.

The nickel coatings, deposited onto the surface of steel specimens passivated in both concentrated nitric acid and an alkaline passivating solution prepared by us, did not break off beyond a portion of the specimen, which was specially treated with graphite. After the load value of 4300-5000 g had been reached, the nickel strip cracked along its cross-section.

The average value of the work needed to break the nickel coating off the surface of the non-passivated specimens amounted to  $2.49 \cdot 10^6$  erg/cm<sup>2</sup>. For the specimens passivated in nitric acid it was  $5.01 \cdot 10^6$  erg/cm<sup>2</sup>, and for those passivated in alkaline electrolyte it amounted to  $4.40 \cdot 10^6$  erg/cm<sup>2</sup>.

During the investigation of the copper and nickel coatings, in the majority of cases the coating was not broken off the surface of the passivated specimens beyond the strip which was mechanically raised. Due to this fact, we have taken the value at which the strip of metallic coating ruptured as the break-off work. In reality, the work needed to break the coating off was greater.

When measuring the work needed to break the copper and nickel coatings off, we have not taken into account the work spent on stretching the coating strip being broken off. This is permissible, however, for comparative tests since we have measured the cohesive strength of deposits of equal thickness.

It is characteristic that the particular values of the break-off work for the nickel and copper coatings, deposited on the surface prepared by usual methods, significantly deviate from the average value. For instance, for the copper coatings the particular values of the break-off work are equal to  $0.21 \cdot 10^6$  and  $0.93 \cdot 10^6$  erg/cm<sup>2</sup>. For the nickel coatings, these values are

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\* Translators note: This is obviously an error in the original, and it should read cm<sup>2</sup>.

$1.37 \cdot 10^6$  and  $4.71 \cdot 10^6$  erg/cm<sup>2</sup>. This nonuniformity is, apparently, caused by a different degree of homogeneity of the surface because of a difference in the character of oxidation when the specimens were in the pickling solution, during washing, and in air. /1958

For the investigation of the cohesive strength of iron coatings, used in repair work, we selected specimens of ST-30 (Grade 30), in a cylindrical form 1.1 mm in diameter, as the objects of our study. The specimens were inserted into openings of the same diameter, drilled in a plate of soft steel measuring 25 mm in width and 5 mm in thickness. The specimens were ground to the size of the opening.

The end planes of the specimens were ground together with the plate, and then, after the usual treatment and passivation in one of the testing solutions, they were subjected to electrolytic iron plating.

The iron plating was carried out in an electrolyte having the content (g/l):  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  - 600, KCl - 100,  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  - 20, ascorbic acid - 0.25; pH = 4-4.5. The temperature of the electrolyte was 20°, the current density  $i_k = 20$  A/square decimeter.

The side surfaces of the plate, its rear part and the ends of the specimens were protected from the iron plating by an alkaline varnish. After an iron layer measuring 1 - 1.5 mm in thickness was deposited, the plate was placed on two supports, with the specimens' ends leading out through the opening between the supports. With the help of a special device, a tray was hung onto the ends of the specimens. The load was set on the tray. The weight of the load, at the break-off instant, determined quantitatively the strength of cohesion between the specimens and the iron deposit.

In order to take into account the effect of the friction of the specimens in the guiding openings, we determined in advance the load needed to break a specimen off. This was done on control specimens before the deposition of a coating. Afterwards, this load was deducted from a general result. Its value constituted 2-4% of the force needed to break the specimens off iron deposits.

The break-off of the specimens, as a rule, occurred in the plane dividing the specimen-electrolytic layer of iron. In individual (rare) causes, the specimens were broken off together with a part of the iron deposited. Such results were not taken into account.

The experiments that we have performed showed that a treatment in various passivating agents before the deposition of a coating in all cases led to a positive effect. Without a treatment in the passivating agents, we could not even measure the cohesive strength, since the iron deposits easily peeled off and came off in scales.

A preliminary anode passivation for 2 minutes in a 30% solution of sulfuric acid with an anode current density of  $i_k = 10$  A/square decimeter made it possible to enhance the cohesive strength of the iron deposition. The

break-off force measured ranged from 5.90 to 6.75 kg (the cohesive strength was 5.90 - 6.75 kg/mm<sup>2</sup>); the average value of the cohesive strength amounted to 6.28 kg/mm<sup>2</sup>. A considerably greater cohesive strength was achieved by means of an anode treatment for 2 minutes in concentrated sulfuric acid with the addition of 20 g/l bichromate at a temperature of 20°, and a current density of 10 A/square decimeter. The average value of the cohesive strength was 10.57 kg/mm<sup>2</sup> (the range was 8.75 - 13.2 kg/mm<sup>2</sup>).

As an example, similar, but less stable, results were obtained during the anode treatment in a mixture consisting of equal volumes of sulfuric acid (specific gravity - 1.82) and phosphoric acid (spec. grav. - 1.39).

The greatest cohesive strength (17.94 kg/mm<sup>2</sup>, the range: 12.9 - 24.3) was reached during an anode treatment for 3 min in a 25% solution of sulfuric acid with  $i_a = 20$  A/square decimeter, followed by immersion in a 20% aqueous solution of hydrogen peroxide until the surface was clear.

On the whole, the preliminary passivation made it possible to use iron plating in cold chlorine electrolytes for the restoration of worn-out machine components. This was confirmed by special industrial studies of iron-plated components.

The application of a preliminary passivation before the aluminization of steel is of a particular interest. The technological process of aluminizing tubes includes the usual preparation (degreasing, etching, pickling) followed by a fluxing treatment for 5-10 minutes in a 2% aqueous solution of a mixture of almost toxic barium chloride and sodium chloride, taken in the ratio 7:3 /1959 at the temperature of 80 - 90°. Further, after drying the tubes were immersed in a bath with melted aluminum heated to the temperature of 690 - 720°.

The break between the fluxing treatment and the aluminizing should not exceed 40 - 60 minutes. After a longer contact with air, the steel surface was covered with a coating of rust. The quality of the aluminum covering was unsatisfactory. An application of a preliminary passivation in a 60% nitric acid or in 3% aqueous solution of chromic anhydride made it possible to exclude the fluxing treatment (Ref. 4).

Aluminum coatings, deposited after a preliminary treatment in passivating agents, were of higher quality, and with a sufficient cohesive strength. Their surface was smooth, shiny, and silvery, whereas the coatings were rough after the fluxing treatment. In addition, it was found that the break between the passivation process and the aluminizing may be as long as 72 hours without injuring the quality of the coating.

These data convincingly show the favorable effect of passivation on the enhancement of the cohesive strength of both electro-deposited coatings and hot coatings.

A passivated surface differs from an etched or pickled one by its greater

homogeneity. The surface of a metal, which was coated with a passive film, preserves its purity until the beginning of electrocrystallization. Correspondingly, a greater number of fine crystals is formed on the surface of the metal, and thus a greater initial uniformity in the distribution of the metal is achieved. The actual interlocking surface between the coating and the base metal turns out to be larger than that obtained with the usual preparation. As a result, one achieves smaller porosity and a greater strength of cohesion with the base metal.

In the deposition of copper coatings on a pre-passivated steel surface, an enhanced cohesive strength can also be explained by their lowered initial porosity. This leads to a decrease in the total flow of the steel pore-copper coating microelements causing the corrosion of the steel base.

The favorable influence of passivation on the quality of hot coatings was earlier discovered also by Gratsianskiy (Ref. 5). Apparently, as in the case of electro-deposited coatings, the thin passive film is reduced, the active metal surface becomes exposed, and this guarantees the strength of the interlocking between the coating and the metal base. It is possible that the reduction of a film has also an electrochemical character in the case of the hot deposition of a coating (Ref. 6).

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